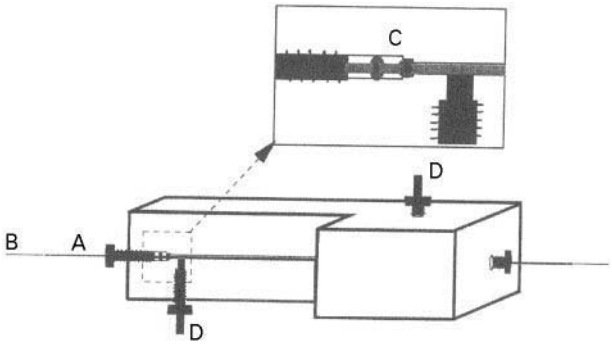

Figure 4 A liquid membrane device for sample preparation. A, hollow fibre (reaching through a hole drilled through the whole block); B, fused silica capillaries inserted in the ends of the fibre; C, O-rings for fixing the fibre and capillaries; D, connectors for the donor channel. (Reprinted with permission from Thordarson E, Palmarsdottir S, Mathiasson L and Jonsson JA (1996) Sample preparation using a miniaturized supported liquid membrane device connected on-line to packed capillary liquid chromatography. *Analytical Chemistry* 68: 2559–2563.)

employed for the analysis of drugs in a matrix of blood plasma.

See also: **III/Membrane Preparation:** Interfacial Composite Membranes; Phase Inversion Membranes.

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Interfacial Composite Membranes

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Introduction

The development of asymmetric cellulose acetate membranes in the 1960s was a breakthrough in membrane technology. These membranes consisted of a thin surface skin layer on a microporous support. The skin layer performed the separation required and because it was very thin fluxes were high. The microporous support provides the mechanical strength required. Following these developments Rozell *et al*. in 1967 described the preparation of the first interfacial (IFC) composite membranes. These membranes have since become the standard for reverse osmosis (RO) and nanofiltration (NF) applications.

IFC membranes have the same asymmetric status of the first-generation cellulose acetate membranes but are made by a very different procedure, shown schematically in **Figure 1**. In a first step a microporous polysulfone support membrane is impregnated with an aqueous solution containing a multifunctional amine. The impregnated membrane is then contacted with a hexane solution containing a multifunctional acid chloride. Because the two solutions are immiscible the reactants can only combine at the membrane interface and so a thin polymer film layer forms at the surface. This layer performs the separation required.

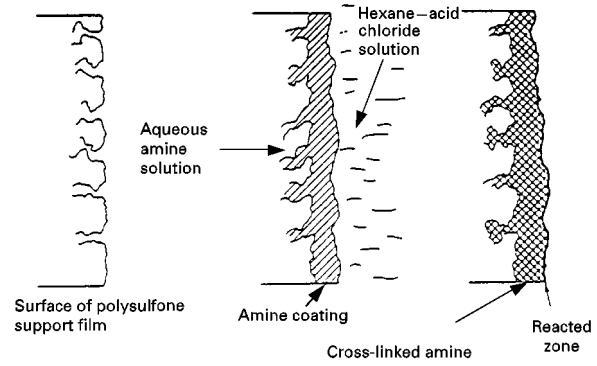


Figure 1 Schematic of the interfacial polymerization procedure. (From Cadotte JE and Petersen RJ (1981) Thin-film composite reverse osmosis membranes: origin, development and recent advances. In Turbak AF (ed.) *ACS Symposium Series 153*, Washington, DC, pp. 305–326.

IFC membrane development can be divided into two time periods. The earlier development from 1967 to approximately 1980 was characterized by work funded through the US Department of the Interior, whereas the majority of the development since 1980 has been industry funded. The early membrane preparations experienced a transition from the use of polymeric to monomeric amine reactants resulting in more durable products. Today the state-of-the-art IFC membrane chemistry consists of cross-linked aromatic polyamides derived from monomeric reactants. A review by Cadotte of composite RO membranes gives an account of the evolution of developments leading up to the commercialization of high performance membranes.

The basic interfacial method of membrane preparation using porous support has changed little since its inception though improvements in reactant chemistry and processing conditions have been made. The laboratory-scale preparation method remains a valuable intiation step in the development of IFC membranes because of its efficiency and simplicity. This method will be given a detailed discussion in the sections which follow.

Interfacial Polycondensation

Early Thin Film Synthesis

The origins of interfacial polycondensation reactions can be traced to Morgan of Du Pont who studied the interfacial polymerization of numerous polyamides and polyesters. He found the Schotten–Bauman reaction of diamines with acid chlorides to be an effective laboratory process, which was termed interfacial polycondensation. In this process, the irreversible polymerization of two highly reactive monomers takes place near the interface of the two phases of nonmiscible liquids, as demonstrated by the model system hexamethylenediamine sodium hydroxide–water/sebacoyl chloride–hydrocarbon solvent to produce Nylon 610. This model system is the basis for the discussion which follows.

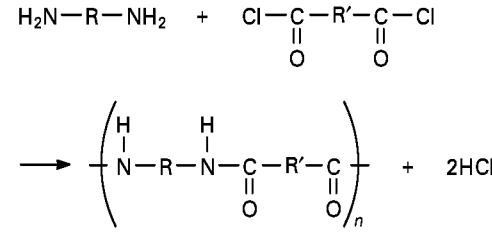
When the two liquid phases containing diamine and acid chloride are brought together and the hydrocarbon or halogenated solvent, etc.) solvent is a nonsolvent for the final polymer, a thin film of the polymer will be formed rapidly at the liquid interface. Generally this polymer is found to be tough and of high relative molecular mass. In a very short time interval equivalent amounts of reactants combine nearly quantitatively, with elimination of hydrogen chloride, and produce a thin film. In Nylon 610 polymerization, the optimal molar ratio of diamine to diacid chloride was found to be about 6.5, indicating the rate-limiting feature of diamine diffusion across the interface and through the growing polymer film. Also noteworthy is the observation that polymer film growth occurs exclusively in the organic solvent phase owing to the extremely low solubility of acid chloride reactants in the aqueous phase. In general it is found that the mass transfer of the diamine is the rate-controlling step at all concentrations of reactants. The variables affecting interfacial polycondenzation determined from experimentation are listed in **Table 1**.

Table 1 Interfacial polycondensation variables

1. Reactivity of amine and acid chloride
2. Partition coefficient of amine water: organic solvent
3. Diffusion rate of amine into organic solvent
4. Concentration of reactants
5. Concentration ratio of reactants
6. Polymer film growth rate
7. Acid chloride hydrolysis rate
8. Polymer film permeability
9. Interfacial tension
10. Acid acceptor type
11. Surfactant type

Mechanism of Interfacial Polycondensation

The mechanism of membrane formation has been studied using the reaction between diamines and diacid chloride and can be generalized in eqn [1]:



[1]

Normally in the interfacial polymerization, sodium hydroxide or other suitable base is added to the aqueous phase as an acid acceptor to neutralize the hydrogen chloride formed and drive the reaction to completion. In some systems excess diamine reactant can serve as the acid acceptor since amine hydrochlorides are highly water soluble and at the same time insoluble in hydrocarbon solvents. In addition to the simple difunctional reactants shown in eqn [1], trifunctional and combinations of di- and trifunctional reactants may be used to achieve the desired degree of polymer cross-linking.

Initially the polymer film grows rapidly; growth then slows and finally a constant film thickness is reached. This is due to the inability of the amine reactant to diffuse through the polymer film to react with the acyl halide. Enkelmann and Wegner

described this process in eqn [2]:

$$\frac{dx}{dt} = K\frac{c}{x} - k'x \qquad [2]$$

where x is the membrane thickness; c is the concentration of diamine; K is the diffusion coefficient of diamine through the membrane; and k' is the rate constant of the inhibiting reaction ($\propto$ acid chloride hydrolysis).

When the limiting thickness x_∞ of the film is reached, $dx/dt = 0$ and eqn [2] simplifies to $x_\infty = \sqrt{Kc}/k'$. The limiting film thickness is therefore proportional to the square root of the diamine concentration. Subsequently, Enkelmann and Wegner established as a solution of eqn [2] the rate law of membrane growth:

$$x' = \frac{x}{x_\infty} = [1 - \exp(-2k't)]^{1/2} \qquad [3]$$

where x' is the reduced membrane thickness. Solving in terms of t (seconds) gives:

$$t = \log\frac{(1-x')^2}{-2k'} \qquad [4]$$

From this equation one can obtain values for early film growth from a period of seconds to over 10 min for more complete growth. It was found from this work that the limiting film thickness depended on both the absolute concentration and concentration ratio of the diamine and diacyl chloride reactants. Enkelmann also showed by X-ray diffraction techniques that in Nylon 610 membranes the polymer chains are ordered perpendicular to the interface. It was also concluded that membrane properties could be regulated by selecting particular reactive monomer ratio and concentrations, solvents and reaction times.

Early IFC Membranes

The IFC Membrane Structure

The development of IFC membranes is a logical outcome following the earlier development of asymmetric cellulose acetate (CA) membranes, as well as the previously discussed interfacial polycondensation work. The CA membrane is comprised of a soluble polymer or blend of polymers of varied cross-sectional morphology with the uppermost surface (skin) forming a permselective barrier. The IFC membrane, which is now the state-of-the art product, contains a microporous support layer of one polymer and a separate permselective skin or thin film of another polymer. The advantage of the IFC membrane is that the chemistry of the all-important permselective thin-film layer can be chosen independently from the underlying porous support material. Asymmetric membranes require polymers that are soluble in solvents necessary for the phase inversion process and this limits the number and type of polymers that can be utilized. Many useful crystalline, semicrystalline, and all cross-linked polymers are thus excluded from asymmetric membrane manufacture. The thin films of IFC membranes are in the range of 20–300 nm thick and when coupled with microporous supports of low hydrodynamic resistance provide membranes with unmatched productivity and solute retention.

NS-100 and PA-300 Membranes

In the discussions of IFC membranes that follow, technical milestones are highlighted with emphasis on commercially significant developments. The early period of membrane development shown in **Table 2** began in 1967 with the investigation of various aqueous diamine and hexane–diacyl chloride interfacial solutions upon polysulfone porous supports by Rozelle *et al.* at North Star Research Institute. These first IFC membranes had low salt rejections, probably due to lack of film integrity since the resultant polymers were not cross-linked. This pioneering work, however, is significant in that the essential elements for the preparation of IFC membranes were demonstrated. Shortly thereafter, in 1970, the first high salt-rejecting IFC membrane, NS-100, was also developed at North Star Research. This membrane was made from polyethylenimine (PEI) in the aqueous solution and toluene diisocyanate (TDI) in the hexane solution. The coated and drained polysulfone support was subsequently dried at 110°C to yield a dry composite membrane with greater than 99% salt rejection on a synthetic seawater feed at 1000 psig (6.9 MPa). A later related membrane, designated NS-101, substituted isophthaloyl chloride (IPC) for TDI as the cross-linker and provided similar results. The selective layers in these membranes consisted of cross-linked polyurea and polyamide films, respectively. The membranes demonstrated high permselectivity but were mechanically delicate and highly vulnerable to attack by chlorine disinfectant.

The sensitivity of early interfacial membranes to chlorine attack was a serious problem that has still not been completely solved. Chlorine is routinely added to water to prevent bacterial growth on the membrane surface. However, exposure to even p.p.m. levels of chlorine destroyed the permselective layer of IFC membranes within a few hours.

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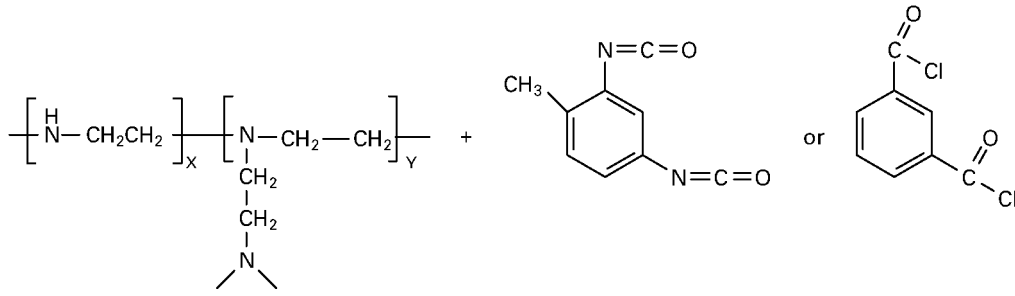
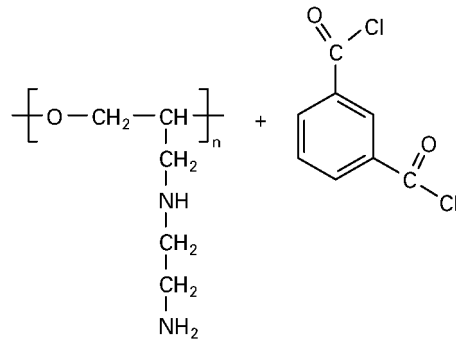
Table 2 Early interfacial composite membrane developments

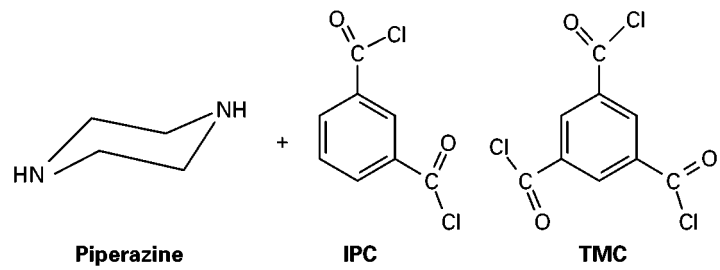
Date	*Development*
1967	First IFC membranes investigated at North Star Research and Development Institute.
1970	NS-100 membrane



1975	PA-300 membrane



NS-300 membrane



Another early membrane developed from a polyamine reactant was the PA-300 membrane by Riley *et al*. at UOP Fluid Systems Division in 1975. The advantage of this polyamide membrane prepared from IPC cross-linker was the lack of residual amines or amide functional groups in the polymer backbone, which exhibited improved chlorine tolerance. The performance of the PA-300 membrane was similar to that of the NS-100 and was the first IFC membrane to be utilized in a large-scale commercial desalination facility located in Jeddah, Saudi Arabia.

NS-300 Membrane

The last example of the earlier generation IFC membranes – the NS-300 – differed from its predecessors in that it was prepared from a difunctional *monomeric* amine, piperazine, and a trifunctional acyl chloride, TMC. This cross-linked polyamide membrane, developed at North Star division of Midwest Research Institute in 1975 by Cadotte *et al*., demonstrated improved tolerance to chlorine compared to its predecessors due to absence of the

vulnerable amidic hydrogen. Later variants of this membrane included addition of the difunctional IPC acyl chloride, which resulted in increased salt rejection and decreased flux. As might be expected, this is probably due to the decrease in residual carboxylic acid functionality resulting from decrease of the trifunctional TMC cross-linker. Another interesting structural aspect of this polyamide is the nearly 90° out-of-plane orientation of the piperazine ring relative to the aromatic ring. This rigid polymer structure containing a high volume geometry may in part account for the high permeability of this membrane.

Contemporary IFC Membranes

Performance Goals

The goal of further membrane development was to maximize solvent passage while at the same time minimizing solute passage. In a typical reverse osmosis desalination application, this means developing membranes with high water permeability yet low salt passage. This effort applies to nanofiltration membranes as well, except in this case passage of monovalent salts and organics of low relative molecular mass is preferred. Since the two performance properties of solvent flux and solute retention are competing, it is found in practice that one generally observes a trade-off in these values with membrane optimization. Both the thin film chemistry and morphology determine its transport properties. Additional goals of recent IFC membrane development include durability, chlorine and other oxidant stability, and fouling resistance.

MPD-Based Membranes

Table 3 lists recent significant IFC membrane developments. Beginning with the wholly aromatic polyamide FT-30 membrane developed by Cadotte at Film-Tec in 1978, it is seen that all of the subsequent membrane examples rely on the aromatic diamine monomer *m*-phenylene diamine (MPD). With the exception of the A-15 membrane, all of the MPD-based membranes provide very high salt rejection and similar water fluxes. Consistent with the general trade-off principle, the A-15 yields higher water flux with commensurately lower salt rejection, making it what is commonly called in the industry a 'loose RO' membrane. The cross-linked aromatic polyamide remains the-state-of-the-art in IFC membrane chemistry. Membranes of this kind are durable, hydrolytically stable, temperature stable, and exhibit high transport properties. A range of commercially successful membranes encompassing nanofiltration, brackish RO and seawater RO applications have been achieved with the basic MPD/TMC reactants. These and other modern IFC membranes are made essentially by the same techniques of interfacial polymerization onto porous polysulfone substrates as were their predecessors.

IFC Membrane Preparation

This section provides general information on how IFC membranes have been prepared and discusses guidelines for others to follow in preparing their own such membranes. The laboratory-scale preparations are discussed in an ordered sequence below with emphasis on techniques commonly practised in the desalination membrane industry for flatsheet IFC membranes. The basic principles of these interfacial techniques are also applicable to the less commercially significant hollow fibre IFC membranes or other composite membrane formats.

Porous Support Preparation

The preferred polymer for use in porous support preparation is polysulfone, a moderately priced material with many desirable chemical and mechanical properties. In addition to strength and temperature stability, it is resistant to hydrolysis and oxidative attack. Its disadvantages, though relatively minor, are its hydrophobicity and lack of solvent resistance. The former property necessitates inclusion of surfactants or wetting agents for some aqueous coating methods used in IFC membrane manufacuture and the latter property limits its applications to ones which are predominantly aqueous or contain nonaggressive solvents such as alcohols and aliphatic hydrocarbons. Nevertheless, polysulfone has been and remains the polymer of choice for the porous support of RO and NF IFC membranes.

Preparation of the polysulfone microporous support may be carried out using laboratory, pilot, or full-scale production equipment. Regardless of scale, all of these procedures involve conversion of a polymer in solvent solution to a porous solid layer in what is called the phase inversion process. As the water in the gelation or solidification bath replaces the solvent, the clear polysulfone solution, or casting solution, is transformed to an opaque plastic layer on to the surface coated. With laboratory preparation this is normally carried out by applying a 14–18% polysulfone solution in *N*,*N*-dimethylformamide (DMF) onto a flat glass plate using a Gardner blade or other suitable device set with a blade gap of 0.13–0.26 mm, then immersing the plate into a small tank of water. For better strength and ease of later processing, it is advisable to do the solution coating onto a calendered polyester fabric or related material attached to the

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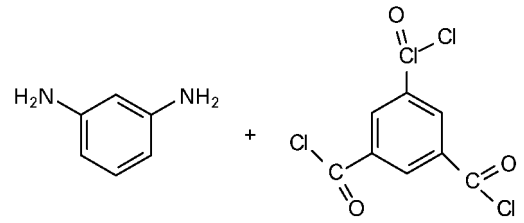
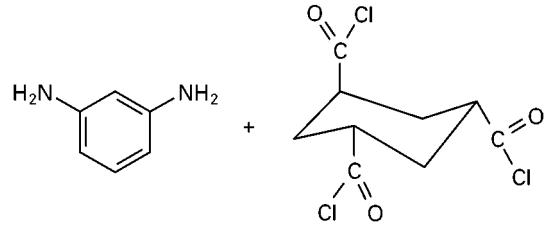
Table 3 Recent interfacial composite membrane developments

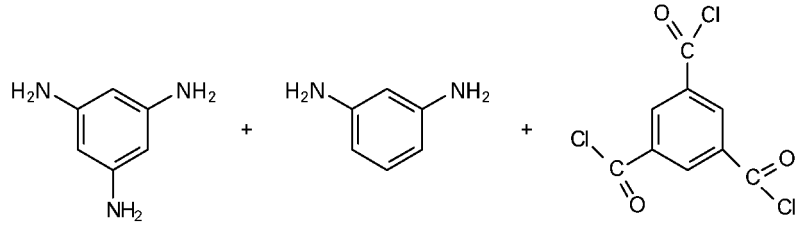
Date	*Development*
1978	FT-30 membrane (US 4 277 344)



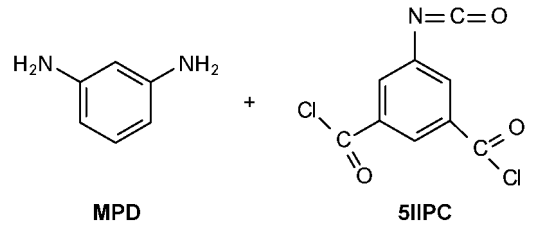
1984	A-15 membrane (US 4 520 044)



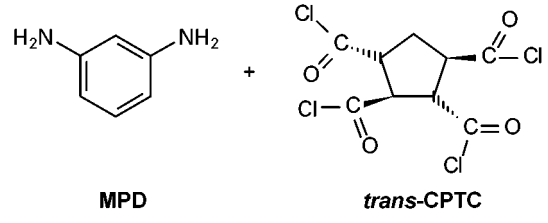
1986	SU-700 membrane (US 4 761 234)



1990	X-20 membrane (US 5 019 264)



1991	NCM membrane (US 5 254 261)



glass plate. After several minutes, immersion time in the water bath to remove all solvent, the newly formed porous substrate is immersed again in a fresh water bath as a final rinse. This batchwise process can be scaled up and carried out as continuous processes employing pilot 1 foot (30 cm) wide or production 40-in wide (~ 100 cm) equipment. The advantages of utilizing the continuous process include not only the obvious efficiency but also better reproducibility in resultant porous support properties. However, it is sometimes necessary to pursue the laboratory batchwise process when experimenting with small quantities of costly new polymers or processing conditions that are not easily implemented on the larger-scale continuous equipment.

A typical polysulfone microporous support used in RO or NF IFC membrane fabrication is, by its pore size designation, an ultrafilter (UF) with surface pore sizes ranging from 0.005 to 0.05 μm. Since this size is an order of magnitude smaller than the interfacial film thickness, it easily supports the film even under operating pressures as high as 1000 psi (6.9 MPa). The thickness of the PS support must be sufficient to cover completely the carrier fabric surface plus irregularities caused by improper calendaring, debris and lack of flatness during the casting operation. In practice the net thickness of the PS layer ranges from 25 to 75 μm and that of the carrier fabric upon which it lies ranges between 75 and 150 μm. Scanning electron micrographs (SEM) of a typical PS porous support cross-section and top view are shown in **Figure 2**A and B, respectively. The anisotropic structure is plainly evident with the finest and most supportive pores residing in the upper surface of the support. The finished PS support is normally stored fully immersed in water or at least damp and protected from dust, debris and biological growth. In some cases it is necessary to include a biocide in the storage water, particularly if it is to be stored a long time. A simplified drawing of a continuous casting machine designed to manufacture PS porous supports in which a carrier fabric is used is given in **Figure 3**. A few additional comments regarding the porous support should be noted. In addition to polysulfone, other similar aromatic polyethers may be used such as polyether sulfone. However, these and other variants are signifiantly more expensive and, except for certain specialized applications, are generally not warranted. The final PS support should be rinsed free of the casting dope solvent otherwise this residual may fuse the porous structure when the IFC membrane is dried.

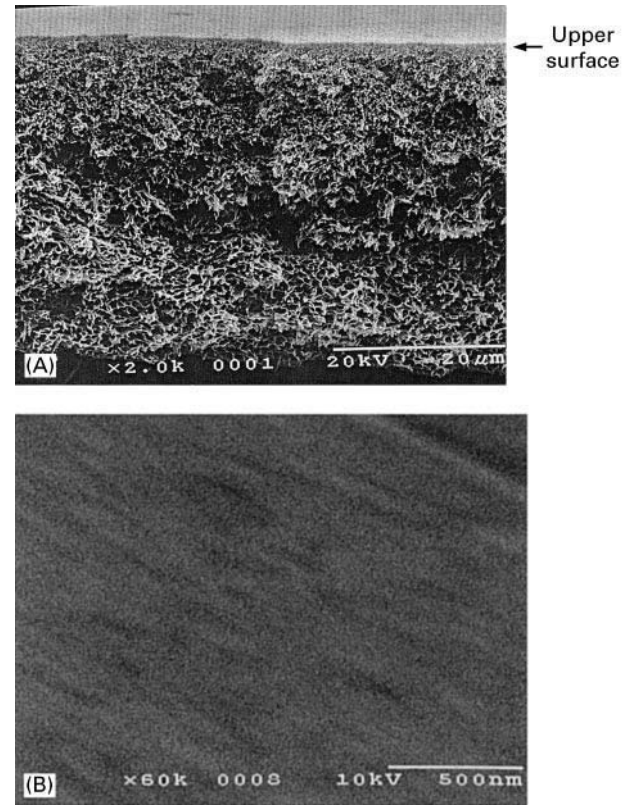


Figure 2 (A) SEM polysulfone porous support cross-section. (B) SEM polysulfone porous support (top view).

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Aqueous Amine Reactant Application

The two basic formulations used in the RO IFC membrane industry contain the diamines piperazine (Pip) or *m*-phenylenediamine (MPD). Because both the reactivity and solubility (partition coefficients) of these two monomers are different, it is necessary to utilize each at different absolute concentrations as well as different concentration ratios with the cross-linker. When using the Pip formulation it is usually necessary to include an acid acceptor such as sodium hydroxide (NaOH) to neutralize the hydrochloric acid by-product of the polyamidization reaction. This is not necessary when using MPD since it is a much weaker base than Pip and used in a higher excess concentration so that, excess MPD serves as its own acid acceptor. It is generally preferred also to include a surfactant in the aqueous amine formula to acid in the wetting and thus even coverage of the PS support. An anionic or neutral surfactant type is preferred.

There are many acceptable techniques for applying the aqueous amine solution to the PS support. Examples of these include dipping, pouring on, spraying, kiss coating, cloth coating, reverse roll coating, etc. A simple yet effective laboratory-scale method involves sandwiching a 6-in. (~ 15 cm) square piece of PS support between two plastic frames using metal clips to hold the two pieces together. An excess of amine solution is then poured onto the top surface of

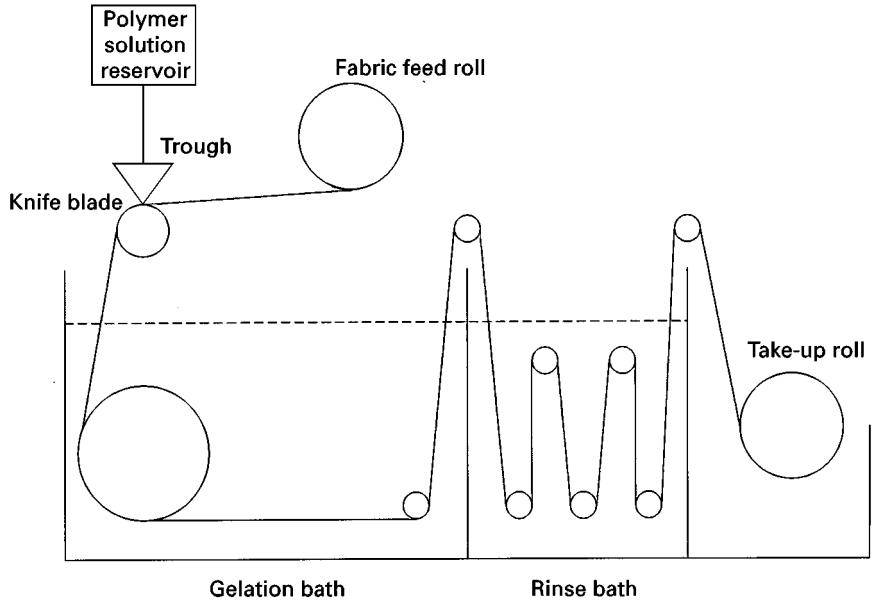

Figure 3 Continuous casting machine for porous support.

the PS support and after a brief time interval is drained off leaving an even, wet layer. Depending on the particular formulation the excess amine may be further removed by rubber roller, squeegee, or air knife. It is important that some degree of wetness remains prior to the contact with the cross-linker solution, otherwise the amine cannot transfer effectively via the water–solvent interface.

Cross-Linker Reactant Application

The choice of solvent for the acyl chloride reactant is dictated by the following requirements:

1. It must completely dissolve the acyl chloride (or other cross-linker) but not react with it.
2. It must be insoluble or virtually insoluble in water.
3. It must not dissolve or swell porous support.
4. It must have a sufficient volatility such that membrane-degrading temperatures are not required for its evaporation.

In practice, the only solvents meeting all of the above requirements are aliphatic hydrocarbons and chlorofluorocarbons (CFCs). There may also be some examples of hydrogenated chlorofluorocarbons (HCFCs) that are acceptable and at the same time are more environmentally friendly than the CFCs. For manufacturing purposes, further restrictions may include preferences for flash point above 100°F and (37.8°C) and low level toxicity. As mentioned previously, the concentration of cross-linker required will be different for the two types of diamines. The concentration of acyl chloride needed for the Pip formulation is approximately five times that needed for the MPD formulation.

The method of cross-link solution application is generally limited to those which do not disrupt the biphasic nature of the interfacial reaction. If excessive disturbance to this step occurs, the growing polymer may be disrupted, leading to thin film discontinuity and ultimately to high salt passage through the defect regions. Dipping, pouring on gently, kiss coating, etc., are effective methods. For the laboratory-scale techniques, excess acyl chloride cross-link solution is gently poured onto the amine solution-coated PS support contained in the frame and kept horizontal for a brief period. The cross-link solution is then drained off vertically, leaving behind the delicate IFC film residing between thin aqueous and solvent layers. The final step involves some form of evaporation of these two solvents as described below.

Drying the IFC Membrane

Since the freshly polymerized thin film resides on a thin layer of water, this layer must be removed for the film to strongly adhere to the PS support surface. It is also desirable to remove the cross-link solvent so that the finished IFC membrane can be safely and conveniently handled in a dry state.

Depending on the volatility of the cross-link solvent and amount of moisture present under the IFC film layer, a temperature range of from ambient to 150°C is required. The higher temperature is a practical upper limit owing to tendency for discoloration and degradation of the IFC membrane. Though many

Table 4 IFC membrane optimization variables: simple approach

Aqueous solution	
1.	Amine monomer concentration
2.	Acid acceptor concentration
3.	Amount of solution applied to porous substrate
Organic solvent	
4.	Cross-link monomer concentration
5.	Cross-link solution contact time with amine solution
6.	Organic solvent volatility
7.	Drying temperature

forms of heating are possible forced air can be used with less heat because of the efficient mechanical effect it has on liquid evaporation. This can be an advantage for IFC membranes that are vulnerable to excessive dehydration. In general, it is found that lower boiling solvents combined with lower drying temperatures often result in membranes with higher fluxes and lower salt rejections than their higher boiling, higher drying temperature counterparts. Of course, longer time periods of drying can be employed in a similar manner with lower drying temperatures to achieve a similar effect, but the choice is ultimately dictated by mechanical and space requirements of the manufacturing equipment. For laboratory scale preparation, it is convenient to use forced hot air devices such as hair-dryers and/or laboratory convection ovens to dry the IFC membrane after the cross-link solution is drained off the frame. Because the thin film is not yet adhered to the PS support excessive air velocity is to be avoided.

The laboratory scale membrane preparation method described in previous sections is now recalled, combining the various steps together: Six inch ($\sim$ 15-cm) square pieces of a polysulfone ultrafilter support are clamped between two Teflon® frames and coated on the upper surface with an aqueous solution of the amine monomer for several seconds; the excess solution is removed by any of the various methods previously mentioned. This freshly coated surface is immediately contacted with the cross-linker–solvent solution horizontally for a period of several seconds then drained vertically for several seconds and finally dried by either forced air and/or convection oven for several minutes. The precise conditions for each of the above steps will depend on the particular type of IFC membrane product that is desired, i.e. NF or RO application, and high productivity or high solute retention, etc., according to the development–performance relationships discussed in the previous sections. A listing of the major IFC membrane preparation variables is given in **Table 4**. SEM pictures of Pip- and MPD-based membranes are given in **Figures 4** and **5**, in which difference in surface roughness is seen. **Figure 6** gives a simplified diagram of the continuous IFC membrane manufacturing process.

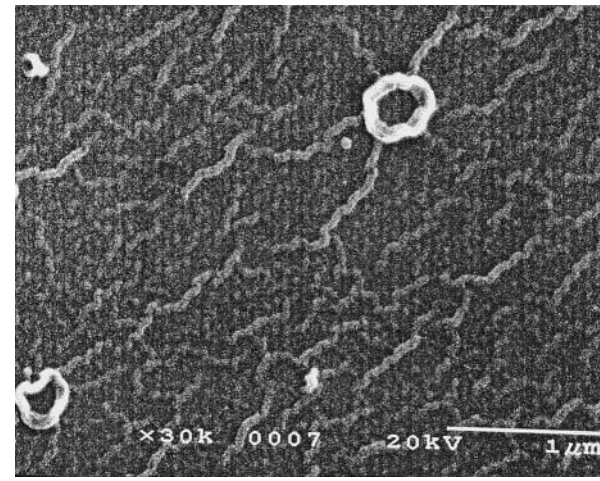

Figure 4 SEM piperazine IFC membrane (top view).

Testing and Optimization

Test Criteria

The membrane performance throughout the optimization process is obtained by testing on various saline or other solute feeds as appropriate for the particular type of membrane being developed. Examples of test feeds commonly used for RO and NF membrane evaluation are shown in **Table 5**. Because these feeds are in some respects arbitrary, one can easily substitute other concentrations of solutes, types

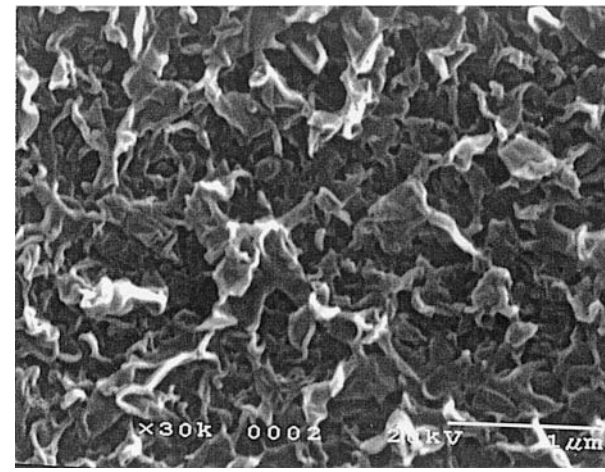

Figure 5 SEM *m*-phenylenediamine IFC membrane (top view).

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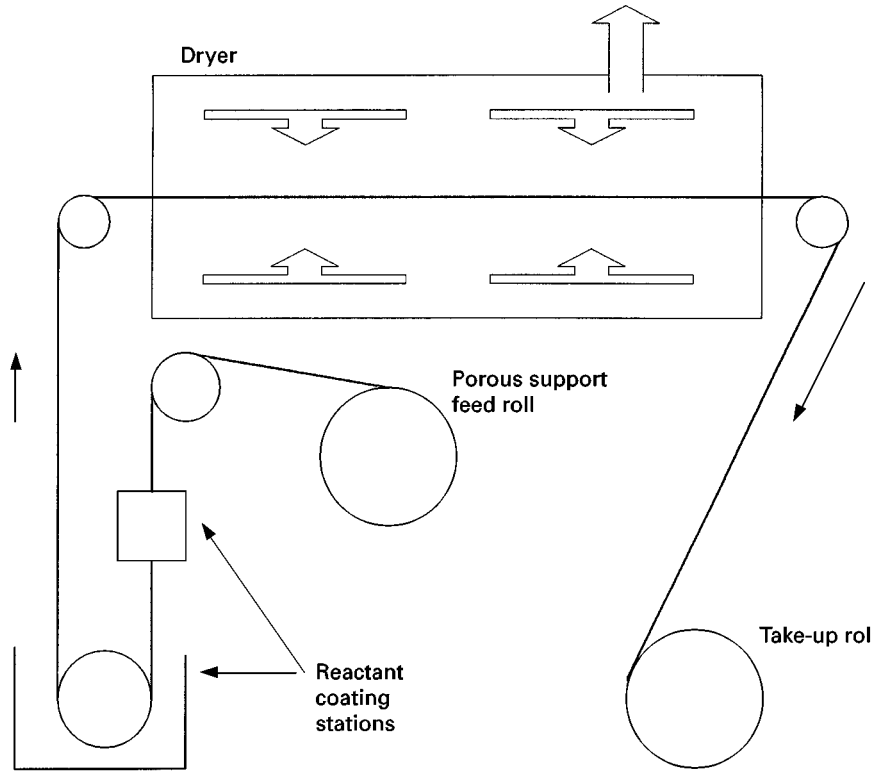

Figure 6 Continuous coating machine for IFC membrane.

of solutes, or test pressures to suit the desired application for the membrane.

The permeate quantity and quality are measured for each membrane sample tested and utilized as performance criteria. In the desalination industry, the former is termed membrane flux, with units of gallons/foot^2-day (gfd) ($\times 40.8$ L/m^2-day) and the latter as salt rejection (%). Flux measurements are made by collecting a volume of permeate under a controlled temperature and time interval. Knowing the active area of the membrane sample and utilizing a temperature correction factor for the viscosity of water, one can calculate the flux normalized to 25°C. Salt rejection is calculated from electroconductivity measurements of the permeates with correction for specific conductance as a function of sodium chloride concentration, or via specific ion probe measurement. Salt rejection is finally calculated as

$$\left(1 - \frac{\text{permeate p.p.m.}}{\text{feed p.p.m.}}\right) \times 100$$

In the case of organic solutes, measurements of permeate and feed are done with a total organic carbon (TOC) analyser with rejection calculated in the same manner as before.

During the membrane development process it is often necessary to rank membranes based upon an objective evaluation. This is difficult because membrane flux and rejection both change. For example, how can a 20 gfd (815 L/m^2-day) 99.0% membrane be ranked against a 15 gfd (611 L/m^2-day)

Table 5 Test feeds for IFC RO and NF membranes

RO membranes			
35 000 ppm NaCl 800 psig	1500 ppm NaCl 150–225 psig	1500 ppm NaCl 1000 ppm $CaCl_2$ 150–225 psig	1500 ppm isopropanol 150–225 psig
NF membranes			
500 ppm NaCl 75 psig	500 ppm $MgSO_4$ 75 psig	500 ppm NaCl 300 ppm $MgSO_4$ 75 psig	500 ppm sucrose 75 psig

99.3% membrane, that is, one with a lower flux but higher rejection. A simple ranking method, if the salt rejection of the membrane is 75% or higher, is to take the ratio of flux/salt passage (F/SP) in which salt passage is simply 100 − salt rejection. This value correlates well with the more sophisticated ranking calculation of A^2/B, in which A is the pure water permeability constant (g mol cm^{-2} s^{-1} atm^{-1}) and B is the salt transport coefficient (cm s^{-1}). In the discussion below, both a simple and a more sophisticated performance optimization example are presented for membrane development.

Simple Approach Optimization

If one has some development experience with a particular amine and cross-linker reactant system such that the workable range of reactant concentrations and processing conditions are at least roughly definable, or if highly optimized membrane performance is not essential, a simplified approach may be pursued. A listing of the recommended minimum number of optimization variables has been given in Table 4. The membrane optimization plan should be carried out in the order shown in this table since it is ordered from highest to the lowest criticality. This approach relies on selecting previously known conditions or educated estimates of some of the variables to be surveyed. The amine monomer concentration experiment would begin by comparing amine concentrations ranging, for example, from x to $3x$ with increments in-between while holding all other variables in Table 4 constant. This requires some discretion in selecting median values of the held constant variables based on prior knowledge. After determining the 'optimum' amine concentration one would proceed in order to the next variable and carry out the next experiment, holding all other variables constant except the acid acceptor concentration that is to be varied. This procedure continues until all the variables have been individually optimized. It is strongly recommended after a once-through optimization to reiterate this process at least once more since new values of many of the variables are likely to have been established. The second time through is likely to result in refinements of both the optimization variable values and the membrane performance.

It should be pointed out that this simple single-variable optimization approach can suffer errors due to interactive variables that can only be optimized in concert. For example, it is likely that, consistent with general principles of chemical reactants, when the amine concentration increases the need for cross-linker increases but so does that for the acid acceptor. In this example there is a three-variable interaction, not merely the two-variable one that the simple method examines. Thus it is often desirable to consider a more sophisticated approach to optimization in which the best combination of variables is found. A multivariable optimization process is offered below.

Self-Directing Optimization Approach (SDO)

In the SDO process, a regular simplex in K variables is constructed. The experiment can be intiated in K variables with $K + 1$ experiments and upon completion of the $K + 1$ experiments, the results are ranked from best to worst. In the case of IFC desalination membranes, ranking is performed using either F/SP or A^2/B calculations made from the flux and rejection results from a specified test feed type and operating pressure. An example of a Placket–Burmann SDO plan containing 11 variables A–K in 12 experiments is presented in **Table 6**. Corresponding to the + and − symbols are high and low levels, respectively, to be selected for each variable A–K. The experiments 1–12 are carried out as one series in a random order. After completion of the first series of 12 experiments, the best eight cases, for example, will have the averages of each of the variables calculated. These average values are then multiplied by 2, then from these are subtracted each of the conditions of the four worst cases. The four new experiments created are then run and ranked against the previous eight best cases as before with subsequent elimination of the four worst cases. This process is repeated several times, each time eliminating the worst cases and creating new ones to be compared with the previous best. Eventually the variables will be found to converge such that the optimization is complete.

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Future Developments

Within the polyamide family of chemistry used in IFC membrane preparation dramatic differences in transport properties can be obtained. It is believed that the thin film polymer chemistry and macrostructure play critical roles in determining these performance differences, thus it is expected that future development will rely heavily on the understanding of polymer structure–property relationships. Though there is relatively little such information available to date concerning membrane polymers, recent computer molecular modelling studies are beginning to show promise. Studies such as these and ones involving the mechanism of solvent/solute transport in permselective polymers will lead to future intelligent design of polymer membranes for specific separation processes. In addition to transport performance, there is still need for improvement in chlorine tolerance and fouling resistance by both RO and NF membranes.

Table 6 Plackett–Burman optimization plan

Exp.	Amine conc.	Acid accept. conc.	Amine applic.	Etc.	A.C. conc.	A.C. time	Sol. B.P.	Etc.	Etc.	Drying time	Etc.	Flux	Rej	A/B	Rank
1	+	+	−	+	+	+	−	+	−	+	−				
2	−	+	+	−	+	+	+	−	−	−	+				
3	+	−	+	+	−	+	+	+	−	−	−				
4	−	+	−	+	+	−	−	+	+	−	−				
5	−	−	+	−	−	+	+	+	+	+	−				
6	−	−	−	+	−	+	−	−	+	+	+				
7	+	−	−	−	+	−	+	+	−	+	+				
8	+	+	−	−	−	+	+	−	+	−	+				
9	+	+	+	−	−	−	+	+	+	+	−				
10	−	+	+	+	−	−	−	+	+	+	−				
11	+	−	+	+	+	−	+	−	−	−	−				
12	−	−	−	−	−	−	−	−	−	−	+				

There are performance gaps in presently available membrane products for the NF area of separations involving species with relative molecular masses ranging from 100 to 3000. It is forseeble that markets will expand for NF membrane applications in high value separations for biotech, chemical, food, and pharmaceutical industries if well-defined relative molecular mass cutoffs can be achieved.

With respect to commercial IFC membrane manufacture, there is a need for improved uniformity and quality of carrier fabrics upon which the porous support is cast. Lack of control here can result in defects that are translated right through the completed composite membrane product. An additional future goal is the development of real-time membrane film integrity and/or performance measurement so that corrections to the process can be made during the course of the manufacture.

See also: **II/Membrane Separations:** Membrane Preparation; Reverse Osmosis; Ultrafiltration.

Further Reading

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Phase Inversion Membranes

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Introduction

Phase inversion is the most versatile technique with which to prepare polymeric membranes. A variety of morphologies can be obtained that are suitable for different applications, from microfiltration membranes with very porous structures, to more dense reverse osmosis membranes, to gas separation and pervaporation membranes, with a complete defect-free structure. **Table 1** gives an overview of the techniques that are commonly applied for the preparation of synthetic polymeric membranes.

Most commercially available membranes are prepared by phase inversion. This is a process by which a polymer is transformed from a liquid or soluble state to a solid state. The concept of phase inversion covers a range of different techniques such as immersion precipitation or 'diffusion-induced phase separation', thermal-induced phase separation, 'vapour-phase' precipitation and precipitation by controlled evaporation. The technique of phase inversion has been known for quite some time; the first paper on the preparation of porous nitrocellulose membranes by phase inversion appeared in 1907.

Table 1 Frequently used techniques for the preparation of synthetic polymeric membranes

Process	*Techniques*
Microfiltration	Phase inversion, stretching, track-etching
Ultrafiltration	Phase inversion
Nanofiltration	Phase inversion, interfacial polymerization [a]
Reverse osmosis	Phase inversion, interfacial polymerization [a]
Pervaporation	Dipcoating [a], plasma polymerization [a]
Gas separation	Phase inversion, dipcoating [a], plasma polymerization [a]
Vapour permeation	Dipcoating [a]

[a]Support layer prepared by phase inversion.

After World War I the number of publications on membrane preparation and characterization increased significantly and led to the development of the first methods for producing porous nitrocellulose membranes in a reproducible way. The 'Membranfiltergesellschaft Sartorius-Werke' in Göttingen was the first company to produce microfiltration membranes on a commercial scale, based on the work of Zsigmondy. This early work on preparation and characterization was reviewed by Ferry in 1936.

Until World War II most membrane research was performed in Germany, but after the war the technology was transferred to USA. In 1960 Goetz developed a new method for the production of porous membranes. Some years later the Millipore Corporation was founded, which commercialized this production method. The membranes were typically microfiltration membranes and were still based on cellulosic materials. It was more than two decades before ultrafiltration membranes were developed. Alan Michaels, founder of the Amicon Corporation, promoted the development of ultrafiltration membranes. Until that time the research was still focused on cellulosics as material but it became clear that due to the limited thermal and chemical stability other materials were required. This resulted in the development of various ultrafiltration membranes from polyacrylonitrile, polysulfone and polyvinylidene fluoride. Today polymeric materials are still the most commonly employed materials both in ultrafiltration and microfiltration. The early companies such as Sartorius and Schleicher and Schuell still exist and have expanded their membrane business to the technical market. Recently the market for the production of drinking water and industrial water from surface water has become important. Here both microfiltration/ultrafiltration and nanofiltration/reverse osmosis are either used as a single separation unit or in combination with each other or with another technique. The nanofiltration and reverse osmosis membranes are either thin film composites or, less commonly, asymmetric phase inversion membranes. In the case of composite membranes a phase inversion mem-

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